Evidence for an Electronic Instability in the Liquid Metal Li(NH$_3$)$_4$

Using high-brilliance x-rays from an undulator source at the Advanced Photon Source, we have carried out high-resolution inelastic x-ray scattering measurements of the low-energy excitations in pure liquid ammonia and in the liquid metal Li(NH$_3$)$_4$ system. In the liquid metal we find a large peak in the structure factor and well-defined excitations that strongly soften in the vicinity of $2k_F$; these indicate we may be near an electronic instability in the system. It is speculated that the structure in Li(NH$_3$)$_4$ spectra may be driven by the tendency of the electrons to order at $2k_F$ and could be an indication of an Overhauser state.

Solutions of alkali metals dissolved in liquid ammonia have been investigated for more than a century because of their many interesting properties. In these systems the outermost electron of the alkali metal separates from the ion, resulting in a free electron and an alkali metal ion. The presence of a free electron makes these systems very different than more familiar solutions (such as salt dissolved in water); the light electron is governed by quantum mechanical effects and cannot be treated classically. We studied a saturated solution of the alkali metal lithium dissolved in ammonia, which has a formula Li(NH$_3$)$_4$. Here each Li$^+$ ion is surrounded by four ammonia molecules, and the remaining electrons travel freely through the system. The Li(NH$_3$)$_4$ system is a true liquid metal down to its freezing point, $T_F = 89$K, but it has a low electronic density.

The ease of changing the electron density (by altering the amount of lithium dissolved), the importance of interactions between the electrons, and the strong coupling to the polar NH$_3$ molecules make Li(NH$_3$)$_4$ a very interesting strongly interacting many-body system. We describe here high-resolution inelastic x-ray scattering (IXS) measurements at $T = 240$K of the low-energy excitations of Li(NH$_3$)$_4$. The system has a Fermi energy E$_F \cong 0.93$ eV and a Fermi momentum k$_F \cong 0.49$ Å^{-1}.

These experiments took place at beamline 3-ID at the Advanced Photon Source. A diamond mono-chromator reflected 21.65-keV x-rays, which were further monochromatized by a four-bounce monochromator and focused onto a 150×350 μm^2 spot. Scattered x-rays were reflected by a temperature-controlled, spherically bent, diced Si (18 6 0) analyzer crystal 6 m from the sample in a near backscattering geometry. The experimental energy resolution was determined to be 2.4 meV using the elastic scattering from plexiglass.

In IXS, an x-ray with a well-defined energy, wave vector, and polarization $(\omega_i, k_i, \hat{e}_i)$ scatters into a new state described by $(\omega_f, k_f, \hat{e}_f)$. An energy $\omega = \omega_f - \omega_i$ and a momentum $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is transferred by the
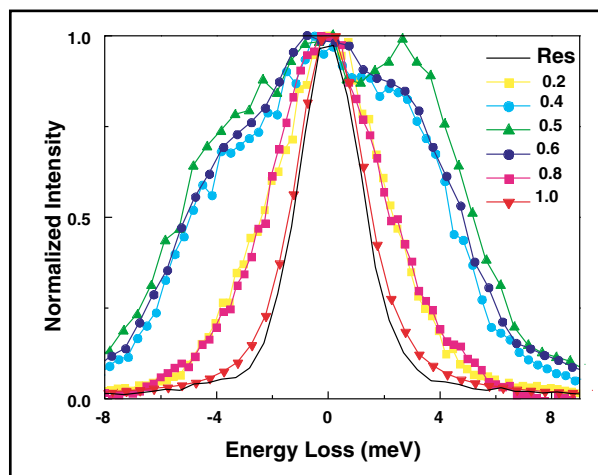

FIG. 1. Low energy excitations in Li(NH$_3$)$_4$ at low momentum transfers (q = 0.2 Å^{-1} to 1.0 Å^{-1}). The phonon modes increase in energy, but then soften to near zero as the wave vector approaches 1 Å^{-1}.

x-ray to the system. This energy and momentum create an excitation in the system, so by studying the energy and momentum lost by the x-ray, we learn about the excitations in the system. Figure 1 shows the spectra of the low energy excitations in $Li(NH_3)_4$ for different values of q. The data have been normalized for comparison. The black curve is the measured instrumental resolution.

The data in Fig. 1 display a dramatic effect. There is clearly a well-resolved collective mode at $q = 0.4$, 0.5, and 0.6 Å^{-1}. The data show that the observed collective mode increases to a maximum near $q = 0.5$ Å^{-1} and then collapses towards "zero" near $q = 2\,k_F \cong 1.0$ Å^{-1}. For more quantitative analysis, we fit the data using a damped harmonic oscillator (DHO) model convolved with our experimental resolution function. Figure 2 shows the results of the fit. At low q the phonons disperse to higher energies, as is expected for a sound-like mode. The mode position has a maxima near $q = 0.5$ Å^{-1} and then is reduced dramatically as q goes to $2k_F$.

For electrons in a uniform positive background (the jellium model), the excitation frequencies are

$$\omega^2(\mathbf{q}) = \frac{\Omega_p^2}{\varepsilon_e(\mathbf{q},\omega)} \quad . \tag{1}$$

Here Ω_p is the ion's plasma frequency and ε_e is the dielectric function for the electron gas. In the low-frequency, long-wavelength limit, static screen-
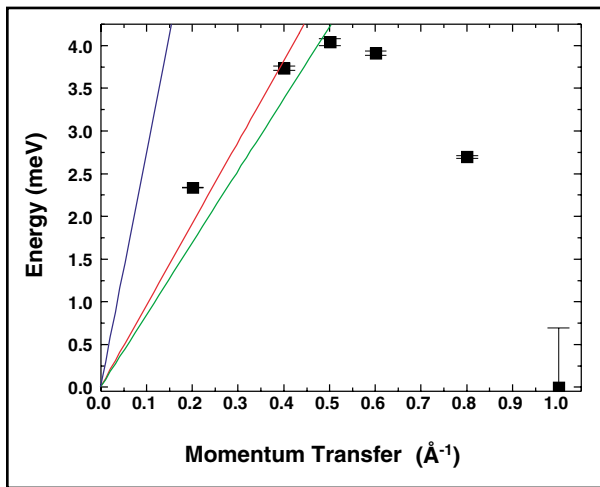
FIG. 2. Fits of the DHO model to the data peaks shown in Fig. 1. Lines are for the ion-acoustic velocity for bare lithium ions (blue), for a $Li(NH_3)_4$ complex vibrating as a unit (green), and for the measured acoustic sound velocity (red).

ing leads to excitations with a linear dispersion. The velocity using Eq. (1) with Thomas Fermi screening is plotted on Fig. 2. The blue line is the velocity expected for bare Li ions, while the green line is for the vibration of a unit where each Li$^+$ is bound with four NH$_3$, which is much closer to the measured results, shown by the red line. From Eq. (1) it is clear that a dramatic reduction in the phonon frequency implies that there must be a strong peak in the dielectric function ε_e near $2k_F$.
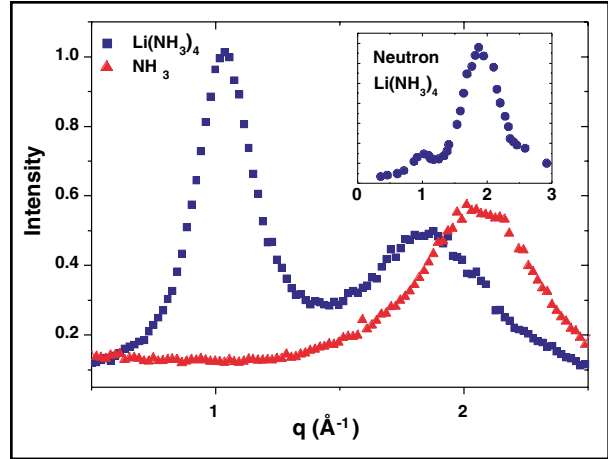
FIG. 3. The structure factor in pure NH_3 and $Li(NH_3)_4$. The inset shows neutron measurements on $Li(NH_3)_4$.

If the observed mode has only softened due to its interaction with the electrons, the minimum in the dispersion curve may hint that we are close to an instability of the ground state. But if the mode truly goes to zero energy, then it would imply a new ground state.

Further indications of ordering are shown in Fig. 3, which displays our measurements of the structure factor for $Li(NH_3)_4$ and pure ammonia. The large, very narrow first peak occurs where our data show the soft collective mode near $2k_F$. Neutron scattering measurements (inset to Fig. 3) of the structure factor in $Li(NH_3)_4$ by Chieux and Bertagnolli [1] show two peaks in the same position as our data, but the relative sizes are very different. The strong peak we observe occurs when Li is added and indicates an additional degree of long-range order for the electron (and also the Li ion) subsystem; if the ammonia were ordering, one would see similar peaks in the neutron and x-ray data, since

the neutron is sensitive only to the nitrogen atoms in the ammonia.

In the early sixties, Overhauser, using a Hartree-Fock description, argued [2] that the ground state of jellium could include ordering at momentum transfers near $2k_F$. Although this topic is quite controversial, some systems, such as the spin density wave state in chromium metal, are probably related to an Overhauser ground state. We believe that the structure in $Li(NH_3)_4$ may be driven by the tendency of the electrons to order at $2k_F$ and could be an indication of an Overhauser state.

In conclusion, we have carried out high-resolution inelastic x-ray scattering measurements of the low-energy excitations in pure liquid ammonia and in the liquid metal $Li(NH_3)_4$ system. In the metal we find a large peak in the structure factor and well-defined excitations that strongly soften in the vicinity of $2k_F$; these indicate we may be near an electronic instability in the system.

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